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(54) **New monoanthraquinone azamethine dyes**

(57) The present invention relates to novel colorants based on monoanthraquinone azamethine derivatives for the mass coloring of polymers, either for polar polymers such as polyamides, polyesters, polycarbonates and ABS; or for non-polar polymers such as polyethylene and polypropylene.

The novel colorants are characterized by a substi-

tuted or unsubstituted annealed aromatic ring system comprising at least one heteroatom.

The novel colorants provide for excellent compatibility with the polymer substrate, excellent heat stability and light fastness.

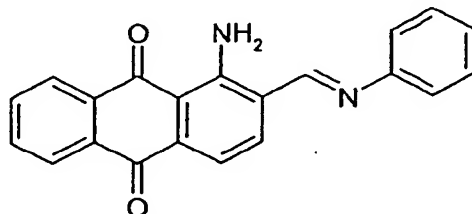
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## Description

[0001] The present invention relates to novel colorants based on mono-anthraquinone azamethine derivatives for the mass coloring of polymers. The novel colorants provide for excellent compatibility with the polymer substrate, excellent heat stability and light fastness as required for mass coloring of polar and non-polar polymers. Polar polymers are for example polyamides, polyesters, polycarbonates and ABS; non-polar polymers are olefin polymers such as polyethylene and polypropylene.

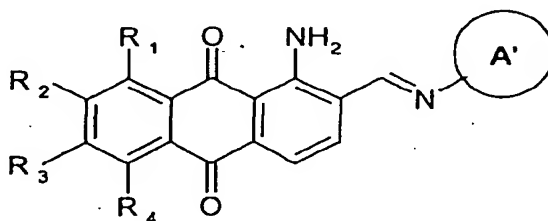
[0002] DE 1285078 (Cassella Farbwerke AG) discloses the use of mono-anthraquinone azamethine derivatives of the formulae given below as pigments for polymer mass coloration. The synthesis of the mono-anthraquinone azamethine phenyl is described starting from the 1-amino-anthraquinone-2-aldehyde.



[0003] Based on own experiments, the mono-anthraquinone azamethine phenyl dye disclosed in DE 1285078 has limited heat stability and limited solubility and therefore only poorly qualifies as polymer-soluble dye. In polymers it provides for rather unattractive brownish red shades and the available colour range is rather narrow.

[0004] The object of the present invention is to provide new heat- and lightfast monoanthraquinone azamethine dyes with excellent compatibility with the polymer substrate and with a wide colour range available, to be useful as polymer-soluble colorants for the mass coloration of polar and non-polar polymers.

[0005] Surprisingly, it has been found that the compounds of the formula (I), wherein the nucleus A' represents a substituted or unsubstituted annealed aromatic ring system comprising at least one heteroatom, provide for the required properties to qualify as polymer-soluble dyes.



(I)

[0006] In formulae (I) the following definitions apply:

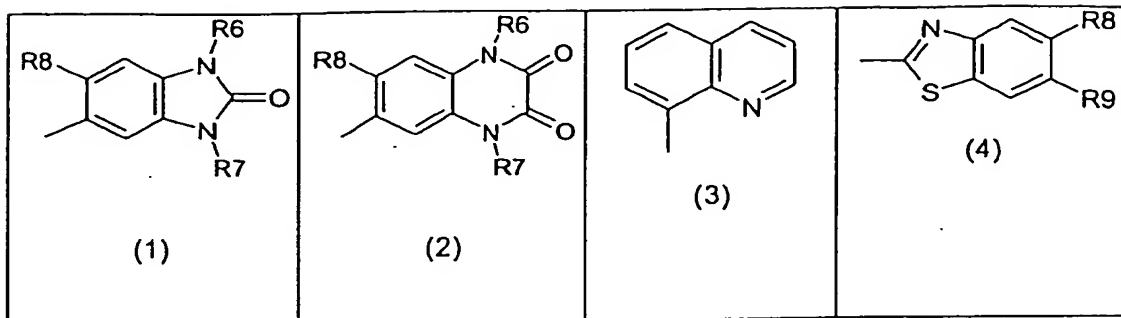
$R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are independently hydrogen, halogen,  $R_{11}R_{12}N$ -,  $R_{12}O$ - or  $R_{12}S$ -, in which  $R_{11}$  and  $R_{12}$  are independently hydrogen,  $C_1$ - $C_6$ -alkyl,  $C_6$ - $C_{10}$ -aryl, in which the alkyl and/or aryl radicals can be substituted by hydroxyl,  $C_1$ - $C_6$ -alkyl,  $C_6$ - $C_{10}$ -aryl,  $C_1$ - $C_6$ -alkoxy,  $C_6$ - $C_{10}$ -aryloxy or halogen.

The nucleus A' represents a substituted or unsubstituted annealed aromatic ring system comprising at least one heteroatom in either the first or the second ring or in both.

[0007] In preferred compounds of the formula (I)

$R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$  are independently hydrogen, chlorine, bromine, methoxy, ethoxy, phenyloxy,  $-NH-C_6H_4-OCH_3$ ,  $-O-C_6H_4-OCH_3$  or  $-S-C_6H_4-OCH_3$

the nucleus A is selected from one of the moieties (1) to (4)



wherein

$R_6$  and  $R_7$  are independently hydrogen,  $C_1$ - $C_{20}$ -alkyl,  $C_6$ - $C_{10}$ -aryl, 2,2,6,6-tetramethylpiperidinyl, in which the alkyl and/or aryl radicals can be substituted by hydroxyl,  $C_1$ - $C_{20}$ -alkyl,  $C_6$ - $C_{10}$ -aryl,  $C_1$ - $C_6$ -alkoxy,  $C_6$ - $C_{10}$ -aryloxy or halogen.

$R_8$  and  $R_9$  are independently hydrogen, halogen,  $C_1$ - $C_{20}$ -alkyl,  $C_1$ - $C_6$ -alkoxy, nitro.

[0008] In more preferred compounds of the formulae (I)

$R_6$  and  $R_7$  are independently hydrogen,  $C_1$ - $C_{10}$ -alkyl,  $C_6$ - $C_{10}$ -aryl, in which the alkyl and/or aryl radicals can be substituted by hydroxyl,  $C_1$ - $C_{10}$ -alkyl,  $C_6$ - $C_{10}$ -aryl,  $C_1$ - $C_6$ -alkoxy,  $C_6$ - $C_{10}$ -aryloxy or halogen.

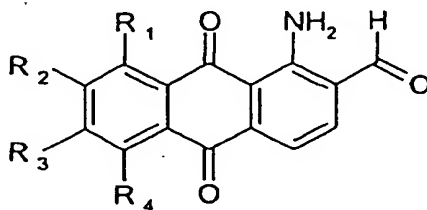
$R_8$  and  $R_9$  are independently hydrogen, halogen or  $C_1$ - $C_{10}$ -alkyl.

[0009] In most preferred compounds of the formulae (I)

$R_6$  and  $R_7$  are independently hydrogen or  $C_1$ - $C_{10}$ -alkyl;

$R_8$  and  $R_9$  are independently hydrogen, chloro or  $C_1$ - $C_{10}$ -alkyl.

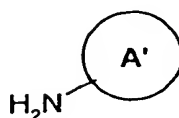
[0010] The present invention also provides a process for preparing the compounds of the formula (I), characterized in that an 1-amino-anthraquinone-2-aldehyde of the formula (II)



(II)

wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are defined as above,

is condensed with an amine or the salt of an amine according to formula (III).



[0011] Suitable salts of the amine of the respective formulae (III) are the chlorhydrate or the sulfate.

The condensation can be conducted without solvent in the melt at temperatures of between 150°C and 300°C, preferably up to 250°C, or in an inert organic solvent at temperatures between 25°C and 300°C, preferably between 80°C and 250°C, in the presence or absence of a catalyst, at atmospheric pressure or under pressure.

[0012] Examples of suitable inert organic solvents are relatively high-boiling aliphatic or aromatic, substituted or unsubstituted hydrocarbons, examples being xylene (mixture), biphenyl, nitrobenzene, chlorobenzenes, chloronaphthalene, glycol ethers, organic acids and acid amides, especially dimethylformamide, dimethylacetamide or N-methylpyrrolidone. Further suitable solvents are alcohols, such as methanol, ethanol or butanol.

[0013] Examples of possible catalysts are inorganic or organic acids, such as hydrochloric or sulphuric acid, benzenesulphonic, toluenesulphonic acid, or acetic acid. The salts of organic acids, such as sodium or potassium acetate, are in many cases also suitable as catalysts.

[0014] The compounds of the invention are eminently suitable for the coloring of melts of synthetic polar and non-polar polymers.

[0015] Synthetic polar polymers are for example polyamide, polyester, polycarbonate or ABS. Preferred polyamides are, for example polycondensation products or addition polymerization products of dicarboxylic acids and diamines, e.g. of adipic acid and hexamethylenediamine, of lactams, e.g.  $\epsilon$ -caprolactam, or of aminocarboxylic acids, e.g.  $\omega$ -aminoundecanoic acid.

[0016] Synthetic non-polar polymers are for example polyethylene, in particular low or high-density polyethylene and polypropylene.

[0017] The polymer melt is mixed with the colorant by conventional methods - for example, in melt spinning, injection molding, extrusion or film blowing machines.

[0018] The novel dyes of formula (I) give red to magenta coloration in synthetic non-polar or polar polymers, such as for example polyethylene, polypropylene, ABS, polyester, polycarbonate or polyamides.

[0019] The novel dyes of the formula (I) are highly compatible with the synthetic polymer substrate and they are extremely stable to the heat stress, which is necessarily part of the coloring of synthetic polymers. Further, the mass-colored substrates display excellent fastness properties, in particular light fastness.

[0020] The novel compounds of the formula (I) are also suitable as colorants in electrophotographic toners and developers, such as one- or two-component powder toners (also called one- or two-component developers), magnetic toners, liquid toners, polymerization toners and specialty toners (literature: L.B. Schein, "Electrophotography and Development Physics"; Springer Series in Electrophysics 14, Springer Verlag, 2<sup>nd</sup> Edition, 1992).

[0021] Typical toner binders are addition polymerization, polyaddition and polycondensation resins, such as styrene, styrene-acrylate, styrene-butadiene, acrylate, polyester and phenol-epoxy resins, polysulphones, polyurethanes, individually or in combination, and also polyethylene and polypropylene, which may comprise further constituents, such as charge control agents, waxes or flow assistants, or may be modified subsequently with these additives.

[0022] The novel compounds of the formula (I) are suitable, furthermore, as colorants in powders and powder coating materials, especially in triboelectrically or electrokinetically sprayable powder coating materials which are used for the surface coating of articles made, for example, from metal, wood, plastic, glass, ceramic, concrete, textile material, paper or rubber (J.F. Hughes, "Electrostatics Powder Coating" Research Studies, John Wiley & Sons, 1984).

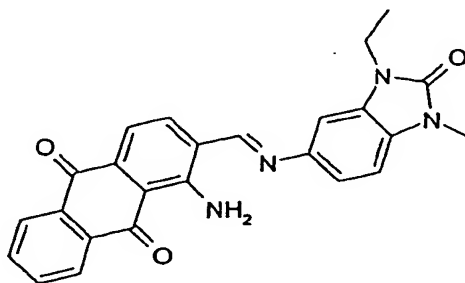
[0023] Powder coating resins that are typically employed are epoxy resins, carboxyl- and hydroxyl-containing polyester resins, polyurethane resins and acrylic resins, together with customary hardeners. Combinations of resins are also used. For example, epoxy resins are frequently employed in combination with carboxyl- and hydroxyl-containing polyester resins. Typical hardener components (as a function of the resin system) are, for example, acid anhydrides, imidazoles and also dicyanodiamide and its derivatives, blocked isocyanates, bisacylurethanes, phenolic and melamine resins, triglycidyl isocyanurates, oxazolines and dicarboxylic acids.

[0024] In addition, the novel compounds of the formula (I) are suitable as colorants in ink-jet inks, both aqueous and non-aqueous, and in those inks which operate in accordance with the hot-melt process.

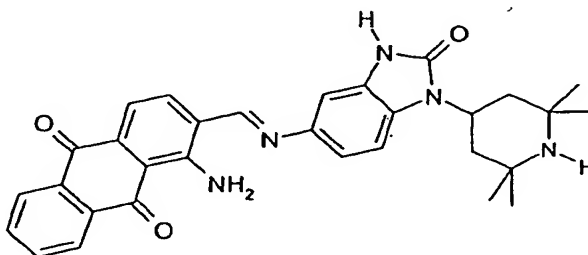
[0025] In the examples below, all parts are parts by weight.

**EXAMPLE 1**

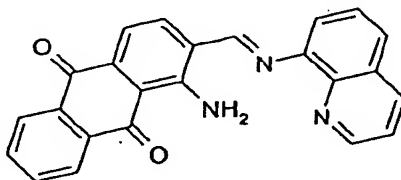
[0026] 14 parts of 5-amino-N,N-diethyl-benzimidazolone and 11 parts of 1-amino-anthraquinone-2-aldehyde are suspended in 100 parts of N,N-dimethylformamide. 0.2 part of acetic acid is added and the red solution is heated to 140°C for 8 hours under nitrogen atmosphere. After cooling to 25°C, the suspension is filtered and the cake is washed successively with N,N-dimethylformamide and methanol and then dried. This gives 15 parts of a violet-colored powder.

**EXAMPLE 2**

[0027] 14 parts of 1-(4'-(2,2,6,6-tetramethyl)piperidiny)-5-amino-benzimidazolone and 11 parts of 1-amino-anthraquinone-2-aldehyde are suspended in 100 parts of N,N-dimethylformamide. 0.2 part of acetic acid is added and the red solution is heated to 140°C for 8 hours under nitrogen atmosphere. After cooling to 25°C, the suspension is filtered and the cake is washed successively with N,N-dimethylformamide and methanol and then dried. This gives 15 parts of a violet-colored powder.

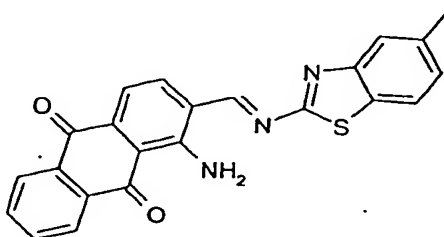
**EXAMPLE 3**

[0028] 14 parts of 8-amino-quinoline and 11 parts of 1-amino-anthraquinone-2-aldehyde are suspended in 100 parts of N,N-dimethylformamide. 0.2 part of acetic acid is added and the red solution is heated to 140°C for 8 hours under nitrogen atmosphere. After cooling to 25°C, the suspension is filtered and the cake is washed successively with N,N-dimethylformamide and methanol and then dried. This gives 15 parts of a violet-colored powder.



**EXAMPLE 4**

[0029] 14 parts of 2-amino-5-methyl-benzothiazole and 11 parts of 1-amino-anthraquinone-2-aldehyde are suspended in 100 parts of N,N-dimethylformamide. 0.2 part of acetic acid is added and the red solution is heated to 140°C for 8 hours under nitrogen atmosphere. After cooling to 25°C, the suspension is filtered and the cake is washed successively with N,N-dimethylformamide and methanol and then dried. This gives 15 parts of a violet-colored powder.

**Use Examples In Polymeric Fibres****USE EXAMPLE 1 (1% of the compound of example 1 in polypropylene fibres)**

[0030] 100 parts of polypropylene in the form of a powder are mixed with 0.1 and with 1.0 part respectively of the dye from Examples 1 in powder form in a drum mixer. After a short time, the powder is uniformly distributed and adheres to the granules. After about 10 minutes, the mixture is dried at 120°C for 16 hours, transferred to a melt spinning machine and following a residence time of about 8 minutes is spun to fibers at 275-280°C under a nitrogen atmosphere. The colored fibers are extremely lightfast.

[0031] All other known synthetic polymers can be mass-colored in the same way, e.g. (HD/LD) polyethylene, polyamides, polyesters, ABS, polycarbonates.

**USE EXAMPLE 2 (0.1% of the compound of Example 1 in polyamide fibres)**

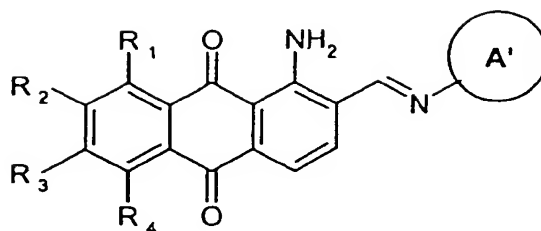
[0032] 100 parts of polycaprolactam in the form of a powder are mixed in a drum mixer with 0.1 parts of compound 1 in powder form. After a short time; the powder is uniformly distributed and adheres to the granules. After about 10 minutes, the mixture is dried at 120°C for 16 hours, transferred to a melt spinning machine and following a residence time of about 8 minutes is spun to fibres at 275-280°C under a nitrogen atmosphere. The violet colored polyamide fibres are extremely lightfast.

**USE EXAMPLE 3 (0.1% of the compound of Example 1 in polyester fibres)**

[0033] Polyester fibres containing 0.1 parts of compound 1 have been prepared according to the following method: the polyester is fused and extruded through a drawing plate at constant rate by gear pump regulation. The spinning machine is heated during 2 hours at temperatures of 260-265°C under pressure of 80 bars. The drawing plate is heated in an oven at 350°C for at least 30 minutes. The obtained fibres are recovered on a bobbin. The obtained fibres provide a strong violet color with excellent light and weather fastness.

**Claims**

1. Compounds of the formulae (I)



(I)

$R_1, R_2, R_3$  and  $R_4$  are independently hydrogen, halogen,  $R_{11}R_{12}N-$ ,  $R_{12}-O-$  or  $R_{12}-S-$ , in which  $R_{11}$  and  $R_{12}$  are independently hydrogen,  $C_1-C_6$ -alkyl,  $C_6-C_{10}$ -aryl, in which the alkyl and/or aryl radicals can be substituted by hydroxyl,  $C_1-C_6$ -alkyl,  $C_6-C_{10}$ -aryl,  $C_1-C_6$ -alkoxy,  $C_6-C_{10}$ -aryloxy or halogen,

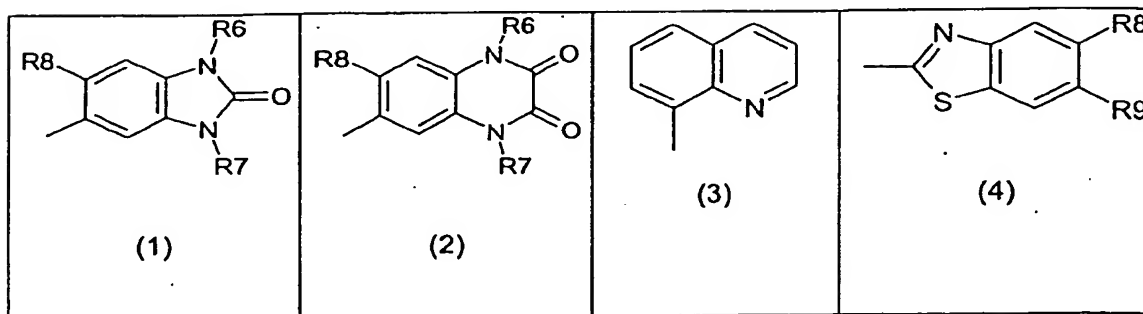
the nucleus  $A'$  represents a substituted or unsubstituted annealed aromatic ring system comprising at least one heteroatom in either the first or the second ring or in both.

2. Compounds according to Claim 1, characterized in that

$R_1, R_2, R_3, R_4$  are independently hydrogen, chlorine, bromine, methoxy, ethoxy, phenyloxy,  $-NH-C_6H_4-OCH_3$ ,  $-O-C_6H_4-OCH_3$  or  $-S-C_6H_4-OCH_3$ , and

the nucleus  $A'$  represents a substituted or unsubstituted annealed aromatic ring system comprising at least one nitrogen atom in either the first or the second ring or in both.

3. Compounds according to Claim 1, characterized in that the the nucleus  $A'$  is selected from one of the moieties (1) to (4)



wherein

$R_6$  and  $R_7$  are independently hydrogen,  $C_1-C_{20}$ -alkyl,  $C_6-C_{10}$ -aryl, 2,2,6,6-tetramethylpiperidiny, in which the alkyl and/or aryl radicals can be substituted by hydroxyl,  $C_1-C_{20}$ -alkyl,  $C_6-C_{10}$ -aryl,  $C_1-C_6$ -alkoxy,  $C_6-C_{10}$ -aryloxy or halogen,

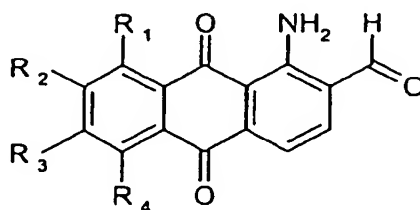
$R_8$  and  $R_9$  are independently hydrogen, halogen,  $C_1-C_{20}$ -alkyl,  $C_1-C_6$ -alkoxy, nitro.

4. Compounds according to Claim 3, characterized in that

$R_6$  and  $R_7$  are independently hydrogen or  $C_1-C_{10}$ -alkyl, and

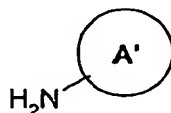
$R_8$  and  $R_9$  are independently hydrogen, halogen or  $C_1$ - $C_{10}$ -alkyl.

5. Process for preparing a compound according to one of claims 1 to 4, characterized in that a 1-amino-anthraquinone-2-aldehyde of formula (II)



(II)

wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are defined as above,  
is condensed with an amine or the salt of an amine of formula (III)



(III)

wherein the nucleus  $A'$  is defined as in claims 1 to 4.

6. Process for preparing a compound according to claim 5, characterized in that the condensation is conducted without solvent in the melt at temperatures between 150°C and 300°C.
7. Process for preparing a compound according to claim 5, characterized in that the condensation is conducted in an inert organic solvent at temperatures between 25°C and 300°C.
8. Use of a compound according to any one of claims 1 to 4 for mass-coloring polar synthetic polymers, preferably polyamides, polyesters, ABS, polycarbonates.
9. Use of a compound according to any one of claims 1 to 4 for mass-coloring non polar synthetic polymers, preferably polyethylene or polypropylene.
10. Mass-colored polymer fibres manufactured from mass-colored polar or non polar synthetic polymers comprising a compound according to any one of claims 1 to 4.





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## EUROPEAN SEARCH REPORT

Application Number  
EP 03 00 2976

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (In Cl.7)
D, A	DE 12 85 078 B (CASSELLA FARBWERKE MAINKUR AG) 12 December 1968 (1968-12-12) * the whole document *	1-10	C09B1/22 C09B55/00
A	DE 10 60 527 B (BAYER AG) 2 July 1959 (1959-07-02) * the whole document *	1-7	
A	US 1 881 697 A (ALBERT KUNZ MAX) 11 October 1932 (1932-10-11) * the whole document *	1	
A	EP 0 023 648 A (BAYER AG) 11 February 1981 (1981-02-11) * abstract; examples *	1,8-10	
A	EP 0 107 492 A (MINNESOTA MINING & MFG) 2 May 1984 (1984-05-02) * page 28 * * page 29 *	1	
A	EP 0 054 217 A (BAYER AG) 23 June 1982 (1982-06-23) * abstract * * page 26 *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C09B
A	EP 0 300 770 A (MITSUI TOATSU CHEMICALS) 25 January 1989 (1989-01-25) * examples 1,3 *	1	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 17 July 2003	Examiner Ketterer, M
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 03 00 2976

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
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17-07-2003

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
DE 1285078	B	12-12-1968	NONE		
DE 1060527	B	02-07-1959	NONE		
US 1881697	A	11-10-1932	DE	436537 C	03-11-1926
EP 0023648	A	11-02-1981	DE	2931710 A1	19-02-1981
			BR	8004883 A	04-03-1981
			DE	3060591 D1	12-08-1982
			EP	0023648 A1	11-02-1981
			ES	8104363 A1	01-07-1981
			JP	56024447 A	09-03-1981
			US	4319025 A	09-03-1982
			US	4389215 A	21-06-1983
EP 0107492	A	02-05-1984	US	4514045 A	30-04-1985
			AU	568096 B2	17-12-1987
			AU	2045583 A	03-05-1984
			CA	1200970 A1	25-02-1986
			DE	3380354 D1	14-09-1989
			EP	0107492 A2	02-05-1984
			FI	833861 A ,B,	23-04-1984
			JP	1723602 C	24-12-1992
			JP	4010514 B	25-02-1992
			JP	59093777 A	30-05-1984
			KR	9104825 B1	13-07-1991
EP 0054217	A	23-06-1982	DE	3046904 A1	15-07-1982
			DE	3164470 D1	02-08-1984
			EP	0054217 A1	23-06-1982
			JP	57123257 A	31-07-1982
			US	4585574 A	29-04-1986
EP 0300770	A	25-01-1989	DE	3851862 D1	24-11-1994
			DE	3851862 T2	24-05-1995
			EP	0300770 A2	25-01-1989
			JP	1103667 A	20-04-1989
			JP	2057187 C	23-05-1996
			JP	7094609 B	11-10-1995
			KR	9104811 B1	13-07-1991
			US	5382465 A	17-01-1995
			US	5252769 A	12-10-1993

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82